



2002 New England Air Quality Study
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Non-Refractory Submicron Aerosol Organic Composition During NEAQS



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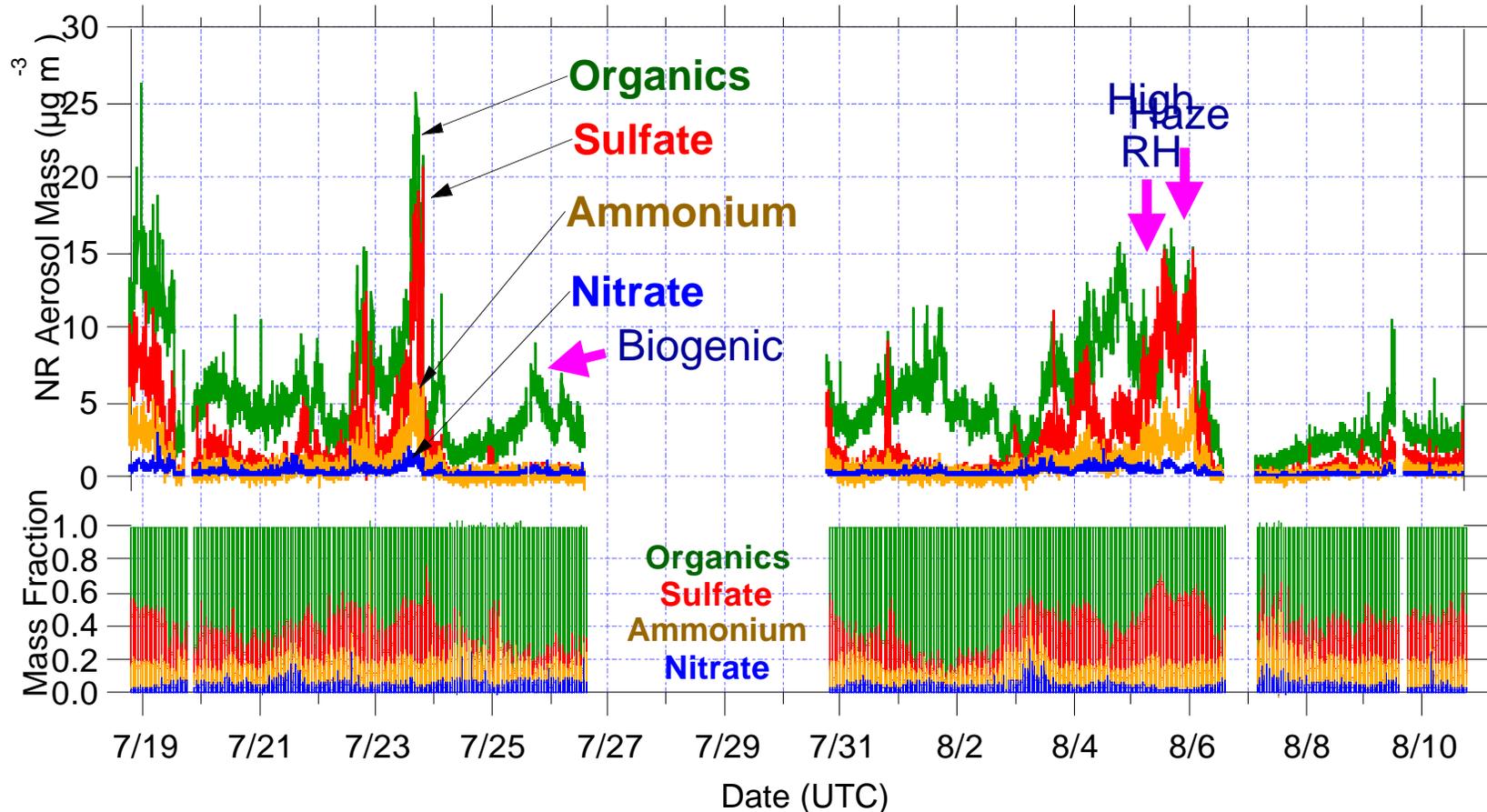
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Outline: What is the Organic Aerosol Mass?

- Overall Aerosol Mass Spectrometer (AMS) Observations
 - Non-refractory (NR) – volatile at 540 C
- Organic Component of the Mass Spectra
 - m/z 44 (CO_2^+) vs. organic mass
- Comparison with Organic Carbon Measurements
- Estimating Organic Mass with Gas Phase Species

- Summary and Implications

AMS NR Mass Loadings



- Mostly organic and ammonium sulfate - organic dominates.
- Sulfate and nitrate mass tracked the organic mass.

Organic and Sulfate Mass

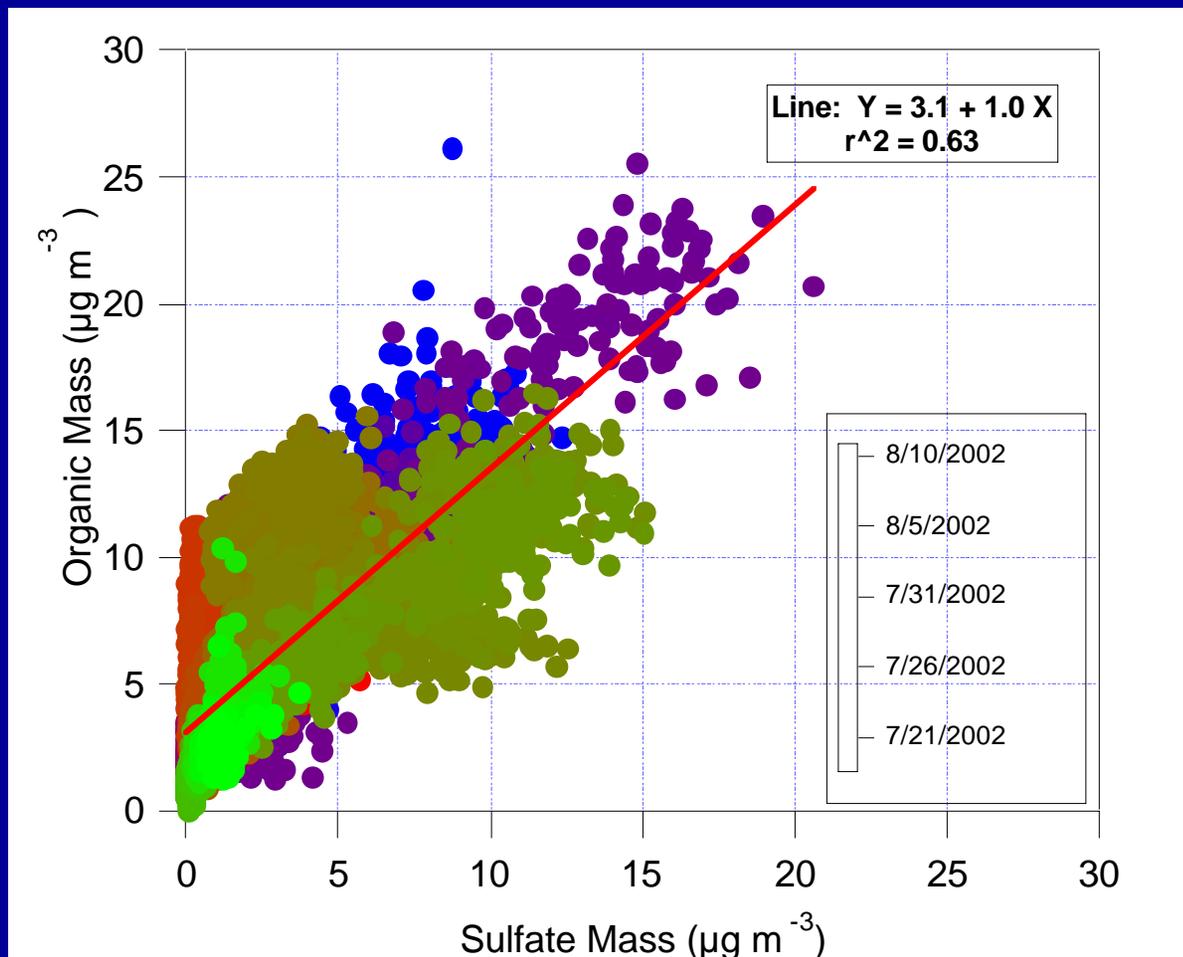
Sulfate and organic mass were correlated.

Formation of organic sulfates?

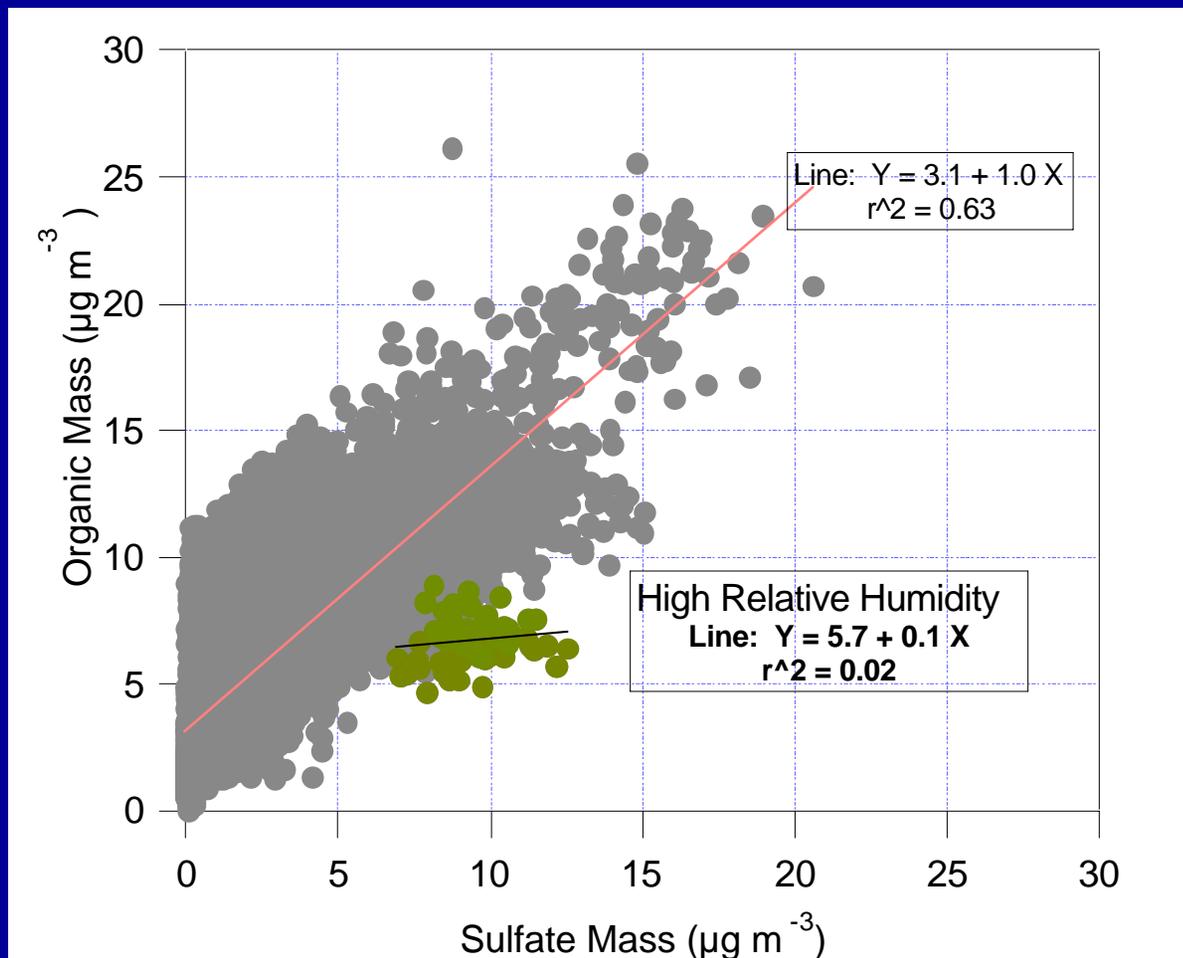
Probably not -
AMS sulfate and ammonium are highly correlated with PILS ($r^2 > 0.85$) and $\text{NH}_4:\text{SO}_4 = 1.7$.

Why is it 1:1?

Synergistic processes?
Not always!



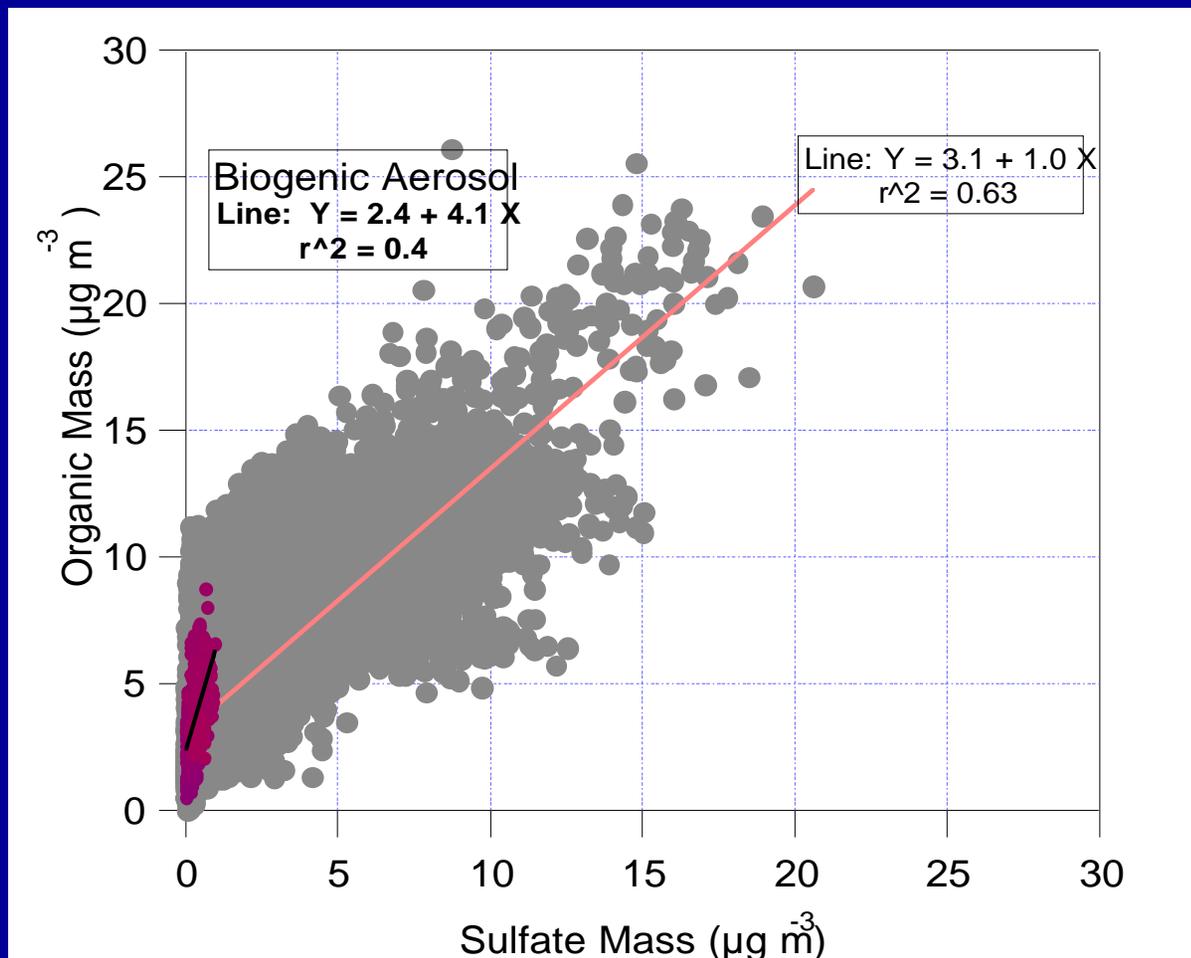
Organic and Sulfate Mass



High relative humidity period on 8/5 has a much lower slope.

Preferential aqueous processing of sulfur dioxide.

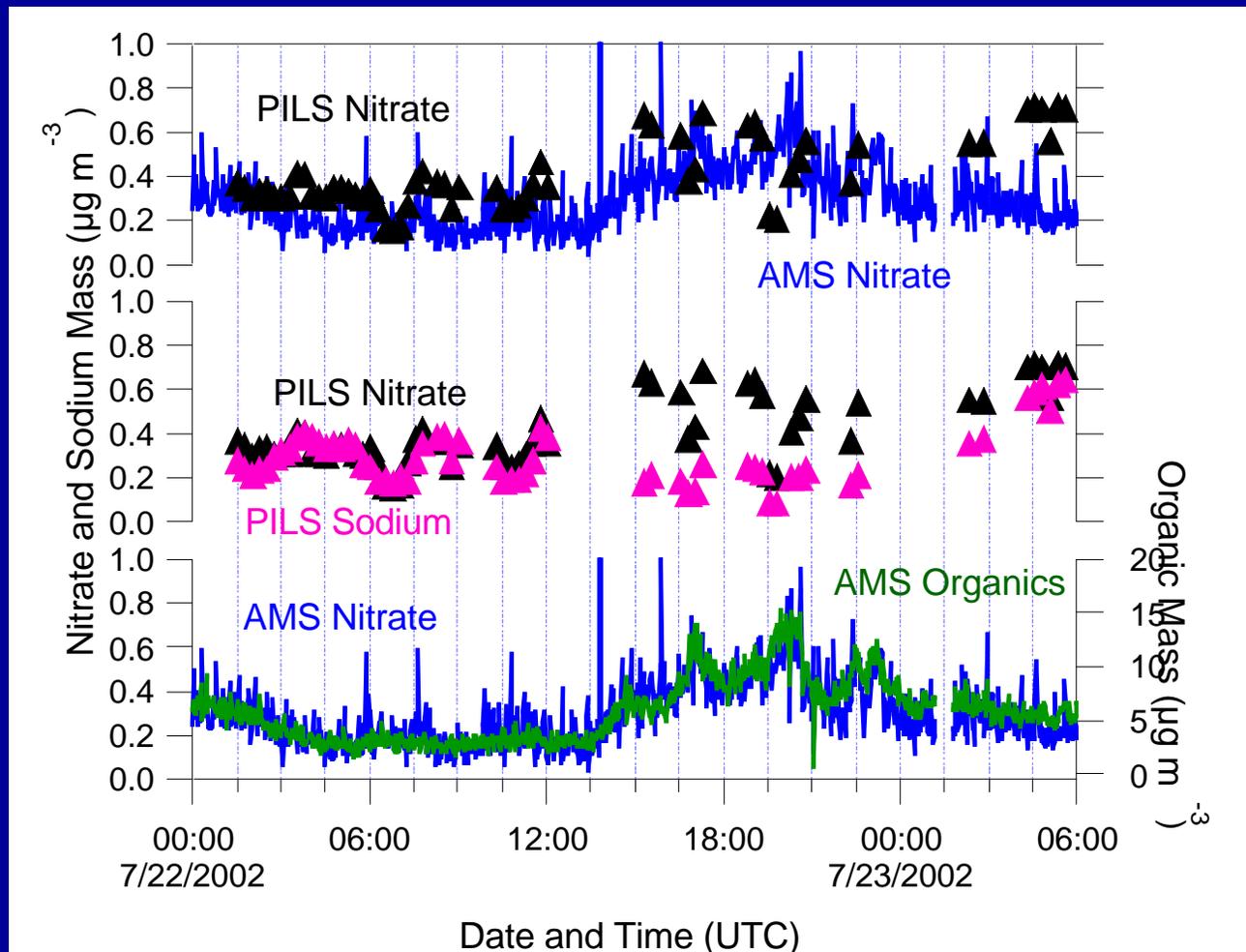
Organic and Sulfate Mass



Biogenic aerosols on 7/25 showed large increases of organics with low sulfate.

Continental air had biogenic volatile organic compounds and low sulfur dioxide (< 620 ppt).

AMS Nitrate and PILS Nitrate

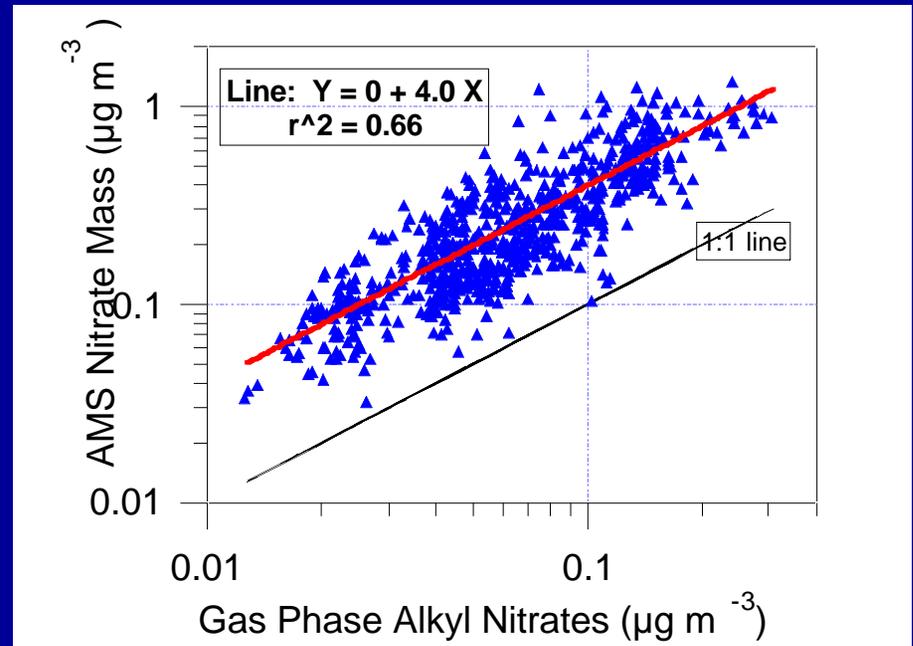
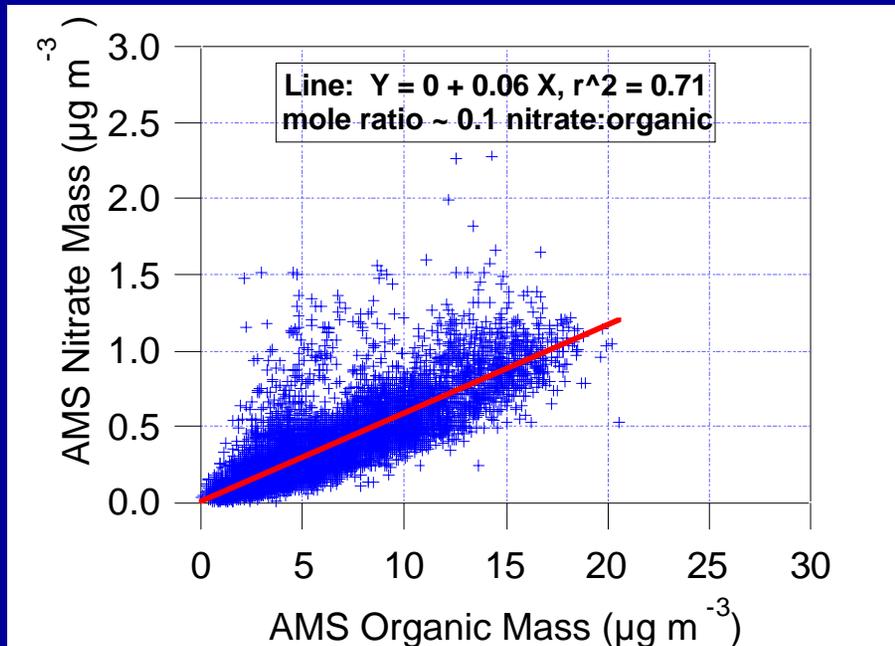


Unlike sulfate and ammonium, AMS and PILS nitrate are not well-correlated ($r^2 = 0.3$).

PILS detects water-soluble species:
ammonium nitrate
sodium nitrate

AMS detects semi-volatile species:
ammonium nitrate
organic nitrate?

AMS Nitrate and Organics



AMS nitrate and organic mass are highly correlated.

AMS nitrate mass and GC/MS gas phase alkyl nitrates are highly correlated.

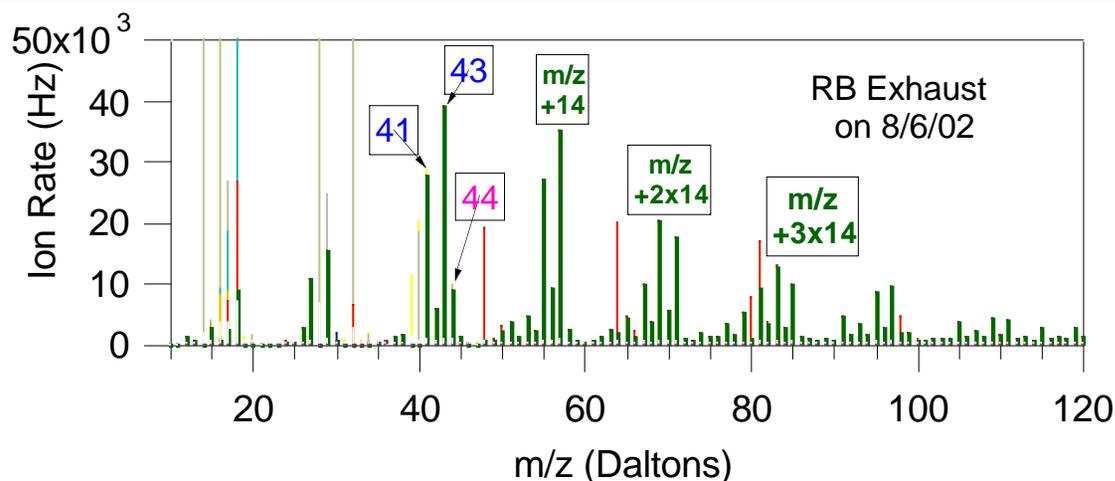
AMS nitrate is probably organic and a significant fraction of the organic molecules could contain a nitrate functionality.

Sample Mass Spectra of NEAQS Aerosols

$m/z\ 41 = C_3H_5^+$

$m/z\ 43 = C_3H_7^+$ or CH_3CO^+

$m/z\ 44 = CO_2^+$



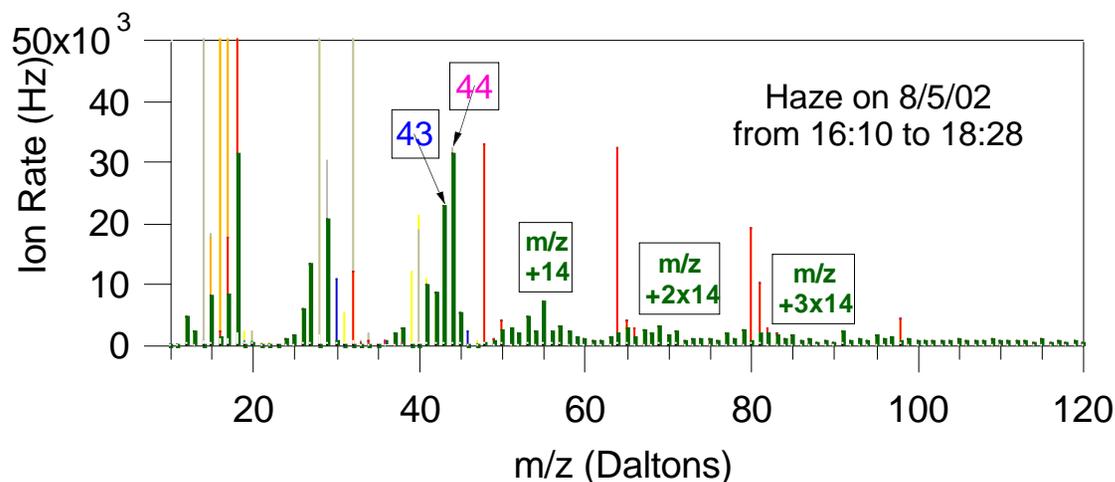
Ron Brown (RB) Exhaust

strong alkyl pattern of $m/z + n \times 14$

$m/z\ 44/\text{organic mass}$ is low (0.026)

small particles

» fresh aerosol



Haze Particles

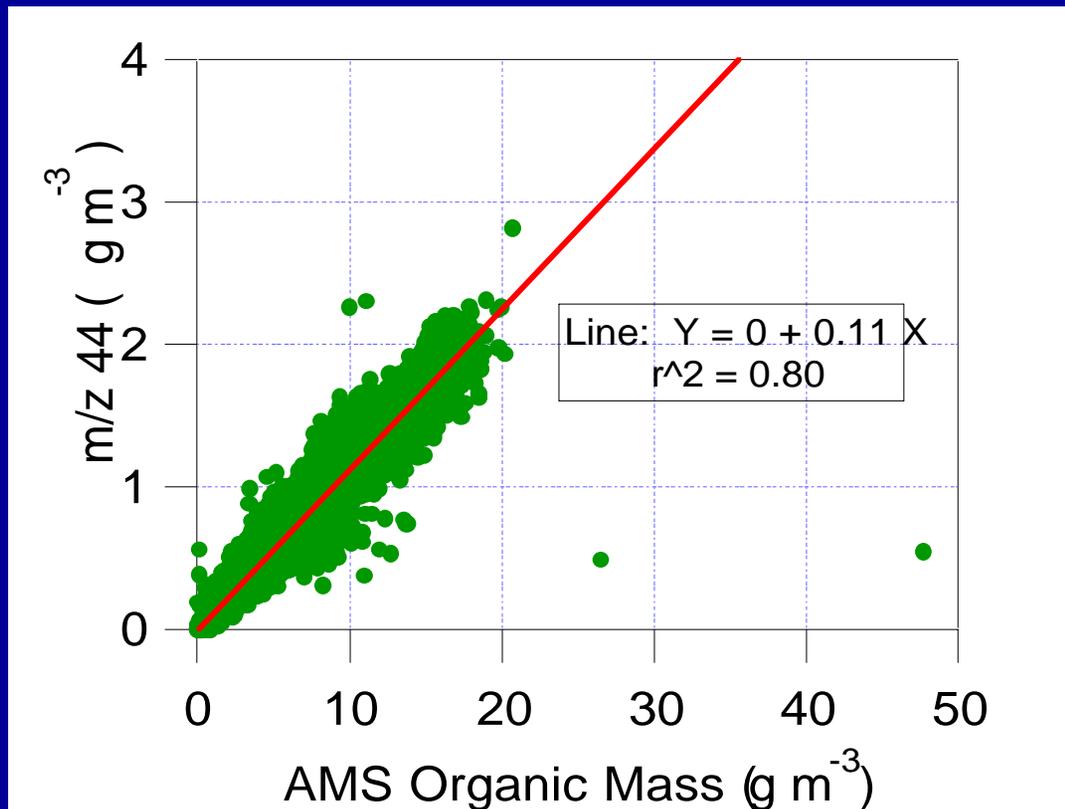
weak alkyl pattern of $m/z + n \times 14$

$m/z\ 44/\text{organic mass}$ is high (0.16)

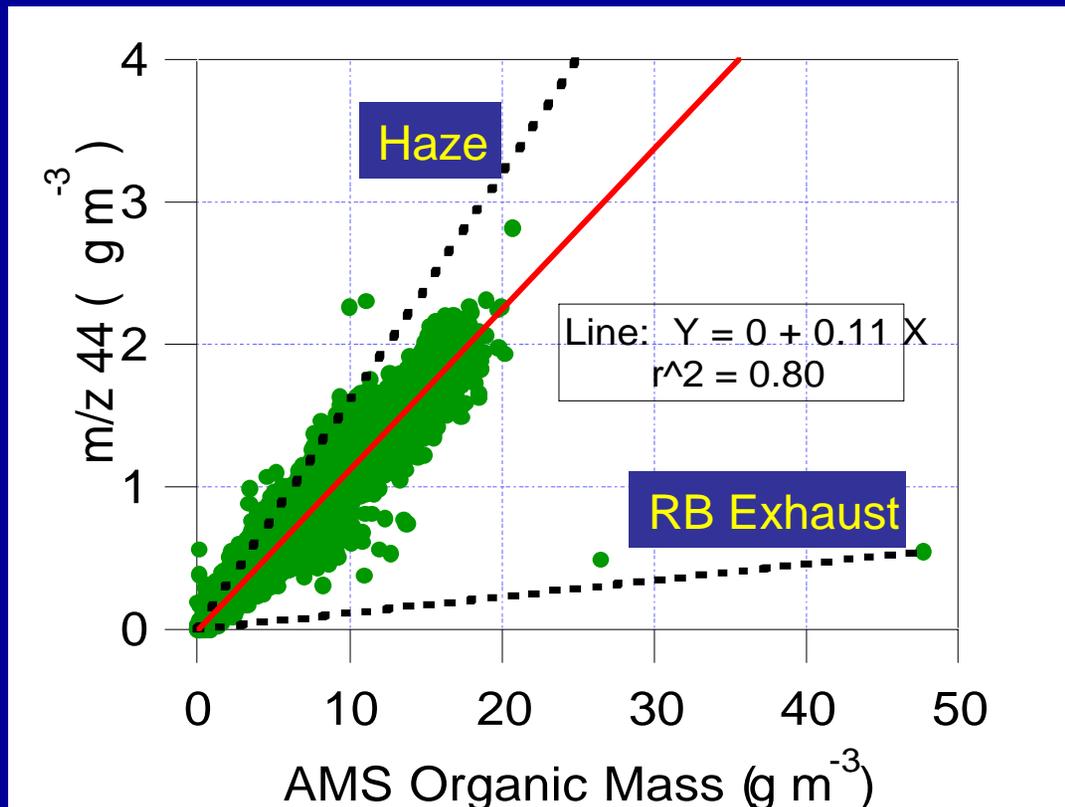
large particles

» aged aerosol

m/z 44 vs. Organic Mass



m/z 44 vs. Organic Mass



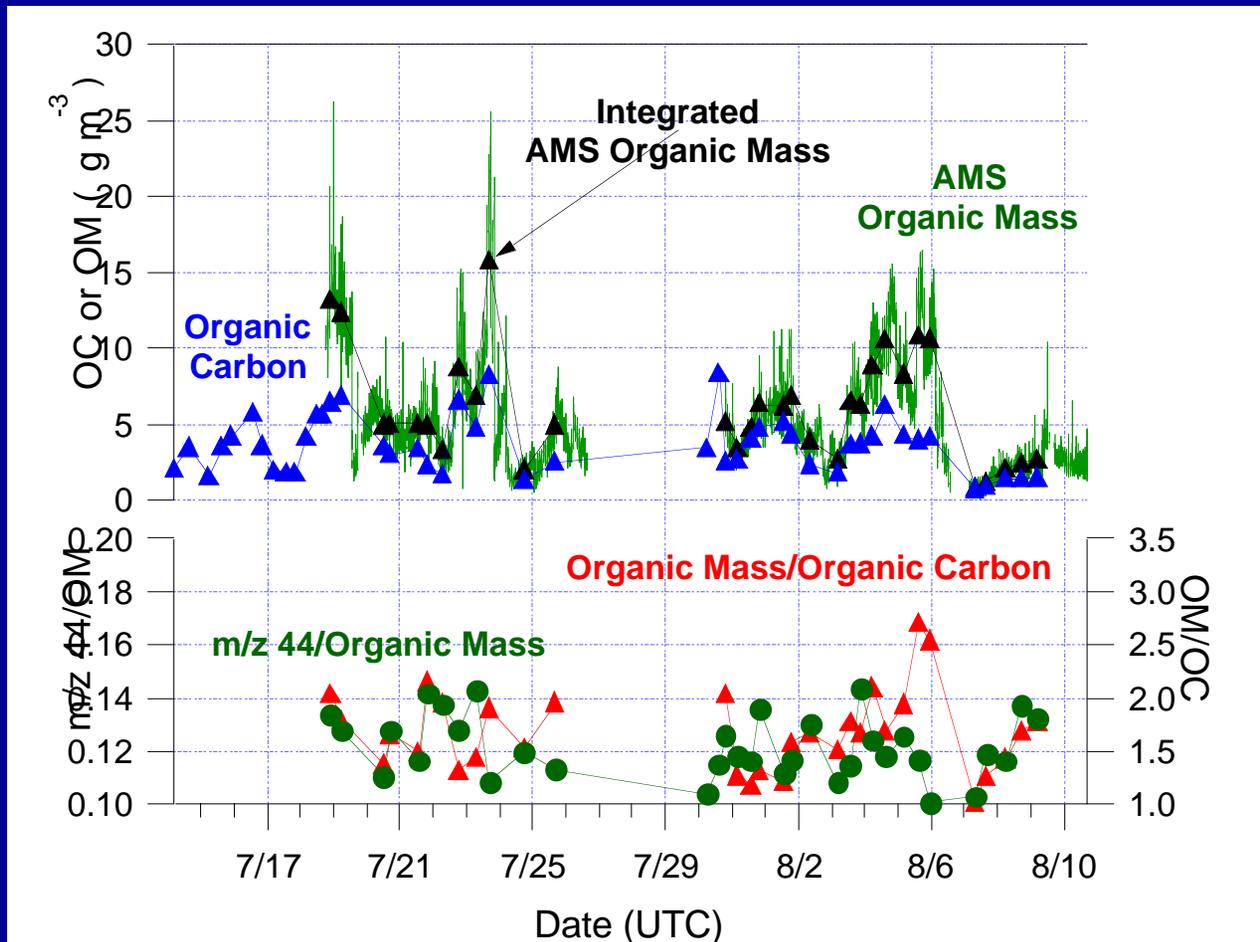
NEAQS average ratio is 0.11.

Haze ratio is representative of oxidized, aged organic aerosol.

RB exhaust ratio is representative of unoxidized, fresh organic aerosol.

NEAQS organic aerosol was generally oxidized (aged).
Fast (a few hours).

Organic Mass and Organic Carbon



Organic Mass and Organic Carbon are correlated ($r^2 = 0.8$).

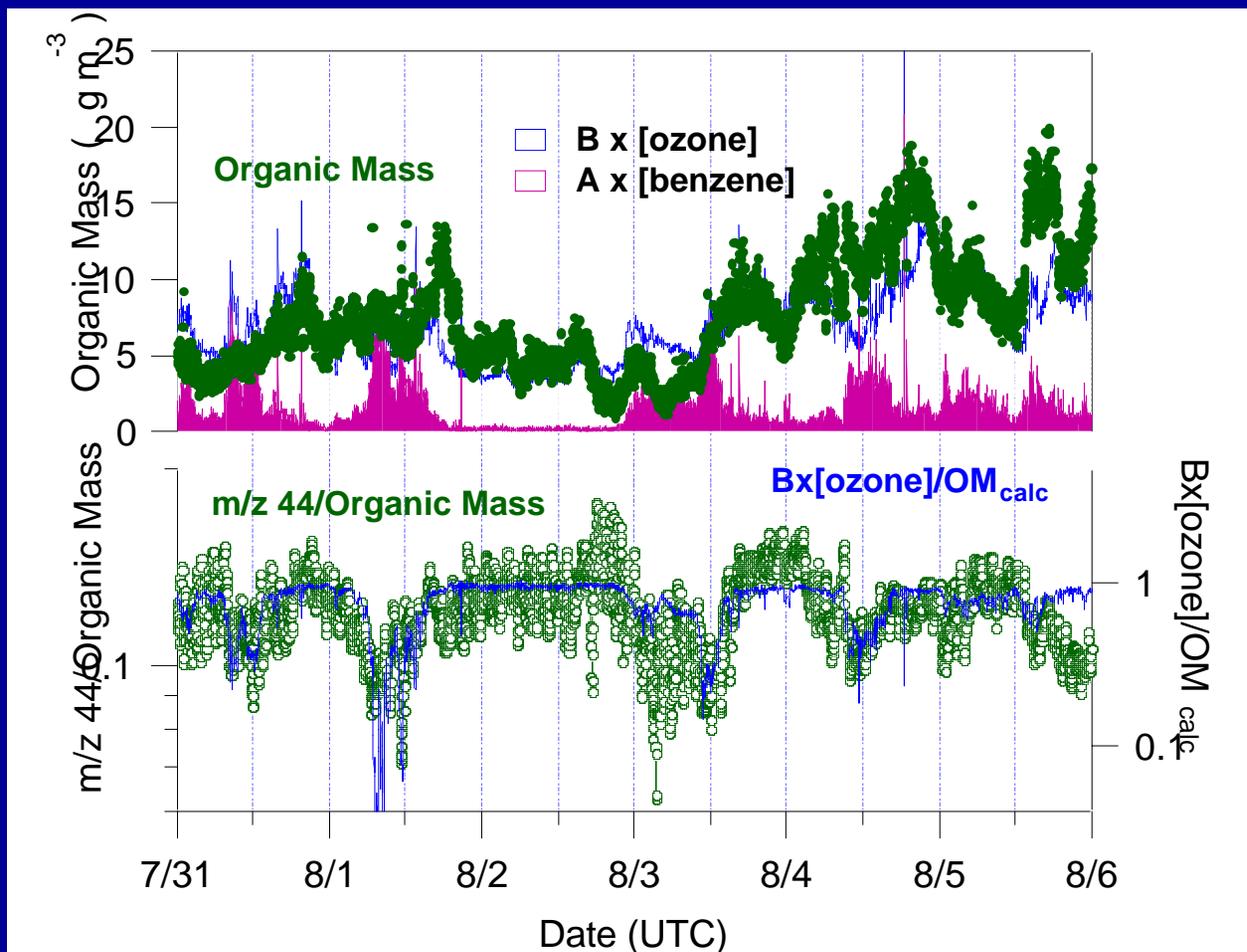
OM/OC averaged 1.7.

OM/OC ratio and m/z 44/organic mass are not always correlated ($r^2 = 0.15$).

Need more comparisons.

Calculation of Organic Mass

$$\text{OM}_{\text{calc}} = \text{constant} + A \times [\text{benzene}] \text{ (primary anthropogenic species)} \\ + B \times [\text{ozone}] \text{ (secondary species)}$$



Organic mass can be estimated with ozone and benzene.

Ratio of ozone to benzene follows similar trend as ratio of m/z 44 to organic mass.

Summary

- Organics and sulfate dominated the AMS non-refractory mass.
- AMS probably detected organic nitrate.
 - 1 out of 10 organic molecules might contain nitrate.
- Used m/z 44 (CO_2^+)/organic mass (OM) to distinguish spectra.
 - Most of the organic aerosol was oxidized.
- AMS organic mass is correlated with organic carbon (OC) data.
- AMS organic mass can be estimated with benzene and ozone.

Implications

- Organic aerosol was mostly aged, not fresh.
 - Rapid processing, sometimes with sulfate.
 - Organic acids – film forming? hygroscopic?
- Organic nitrate may be an important aerosol species.

Acknowledgements

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- Jose Jimenez and other AMS users – data interpretation.